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THE ROLE OF SURFACE STATES IN THE FORMATION OF A SCHOTTKY BARRIER AT A METAL/GALLIUM ARSENIDE CONTACT

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THE ROLE OF SURFACE STATES IN THE FORMATION OF A SCHOTTKY BARRIER AT A METAL/GALLIUM ARSENIDE CONTACT*

G. B. Seyranyan, Yu. A. Tkhorik

Lately significant progress has been made in understanding the mechanisms /34** of the conductance of a current through a metal/GaAs contact and the causes for deviations in the contact from predictable characteristics of classic diode theory. This, however, cannot be said of factors determining barrier height. Despite a number of studies both for a surface sheared off in an ultrahigh vacuum [1] and for an etched GaAs surface [2-5], we cannot consider as explained the relative proportion of contact potential difference (CPD) and that of surface /35 electron states (SES) in the formation of a Schottky barrier.

For example, Mead [6], interpreting experimental results of [1], concludes that the Fermi level is stabilized on an atomically-pure semiconductor surface by a zone of surface electron states (SES), while the authors of [7] reach practically the opposite conclusion from these same experimental results. Other works [2], having deposited the metal on an actual GaAs surface (electrochemical deposition), also indicate rigid stabilization of the Fermi layer by a Tamm type SES. At the same time Rhoderick [8] emphasizes that on an etched surface a stronger dependence of barrier height on the work function of the metal φ_m must be expected than on an atomically-pure semiconductor surface.

The literature also lacks agreement in relation to anisotropy of barrier height, i.e. its dependence on crystallographic orientation of the semiconductor surface [2, 8, 9]. We recall that the anisotropy plays an important role in the intrepretation of experimental data and their comparison with theoretical models [2, 8].

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In order to explain rules in the formation of a Schottky barrier at a metal/GaAs contact this work studied barrier height in relation to the nature of the metal and the crystallographic orientation of GaAs [(111)A, (111)B and (110)]. Along with the metals normally used to produce a linear metal/GaAs contact (Sn, Ni, Ag, Au), Ca and Mg were also used, which significantly broadened the range of the work function of these metals.

SAMPLE PREPARATION

Plates of n-type GaAs (donor concentration N_d = * 16 cm^{-3}, electronic mobility at room temperature * $cm^2/V \cdot sec$) oriented to planes (111) and (110) were etched in a mixture of nitric and fluoric acids and washed in twice-distilled water, after which tin was fused at 400°C to produce ohmic contacts. After the contacts were covered with a chemically stable varnish the plates were etched in a polishing etchant * $:H_2O_2:H_2O=3:1:1$. The etching process was ended by cleaning in ethyl alcohol, then the plates were exposed for several minutes in a complexing agent based on sulfuric and tartaric acids to remove the oxide from the surface [2] again washed with ethyl alcohol and placed in a vacuum chamber. After an effective vacuum of $5 \cdot 10^{-6}$ torr was reached, the GaAs plates were heated to 100-120°C and then their temperature was reduced to 50-100°C and the contact metal deposited. Ca and Mg contacts, in view of their easy oxidizability, were protected by a gold film, which was applied to the metals immediately after deposition. Control experiments showed that the application of a protective film to rather thick Ca and Mg layers did not change the parameters of the contacts.

RESULTS

Volt-ampere characteristics (VAC) were well described by Schottky according to diode theory, according to which even the barrier is due to thermoelectronictric emission:

$$I = AT^2 e^{-\frac{\varphi_B}{kT}} \left(e^{\frac{eU}{nkT}} - 1\right), \tag{1}$$

where φ_B is barrier height; n is the parameter for these diodes equal to 1.05±0.03, A = 4.4 $a/cm^2 \cdot deg^2$. The nearness of parameter n to one indicates that the combination of chemical and thermal treatment of the surface, used in /36

*Translator's note: Foreign text missing.

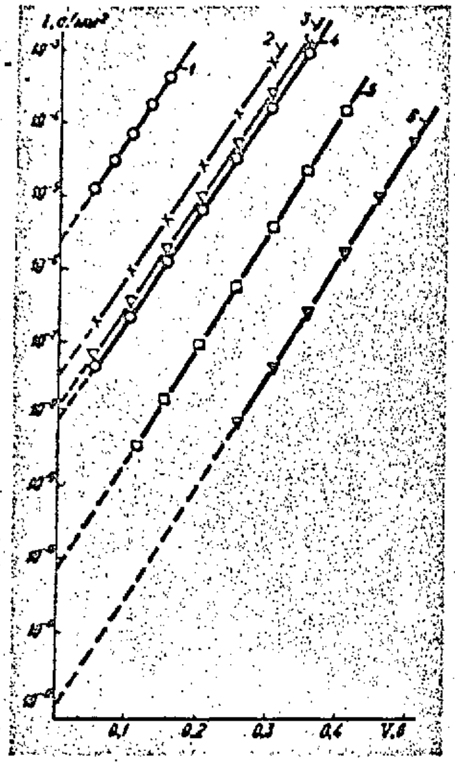

Fig. 1. VAC lines of metal/GaAs (111)A diodes: 1 — Ca; 2 — Mg; 3 — Sn; 4 — Ni; 5 — Ag; 6 — Au.

this work, makes it possible to reduce the thickness of the oxide layer on the semiconductor surface so much that it has no marked effect on the conductance of a current through the contact [10]. VAC lines of metal/GaAs diodes (111)A are given in Fig. 1. It can be seen that VAC essentially depend on the nature of the metal. Extrapolation of VAC (Fig. 1) to zero drift makes it possible to determine saturation currents and, therefore, calculate the height of Schottky barrier φ_B. Barrier height was also determined from volt-farad characteristics (VFC) of contacts, produced at a frequency of 1.2 Mc (typical VFC are given in Fig. 2). The dependence of $1/c^2$ on U usually maintained linearity to 2 V. The table gives heights of the Schottky barrier in electron volts, determined from VAC (φ_{Bi}) and VFC (φ_{Bc}). As in other works [2, 3], calculated values of φ_{Bc} slightly exceed φ_{Bi}, which is usually connected with the presence of deep impurity levels in GaAs [3, 11]. Fig. 3 shows the dependence of barrier height for metal/GaAs (111)A diodes on the work function of the metal. Along with results of this work, Fig. 3 gives experimental points taken from works [1-3].

As heat treatment can affect the electrical characteristics of contacts [3], the dependence of barrier height on the temperature of GaAs was studied in the deposition of metal. It was shown that in the temperature range 25-120°C, barrier height has practically no dependence on the temperature of deposition with the exception of Sn-GaAs contacts, for which a very slight increase of barrier height was observed and deterioration of VAC with a lowering of temperature during the metal deposition process.

Orientation	Ca		Mg		Sn		Ni		Ag		Au	
	φ_{Bi}	φ_{Bc}	φ_{Bi}	φ_{Bc}	φ_{Bi}	φ_{Bc}	φ_{Bi}	φ_{Bc}	φ_{Bi}	φ_{Bc}	φ_{Bi}	φ_{Bc}
(111)A	0.53	0.56	0.63	0.70	0.65	0.72	0.67	0.72	0.80	0.85	0.90	0.95
(110)	0.52	0.56	0.64	0.70	0.67	0.77	0.74	0.79	0.85	0.91	0.90	0.97
(111)B	0.46–0.51	--	0.68	0.75	0.68	0.77	0.87	0.94	0.87	0.92	0.93	0.99

DISCUSSION

Dependence of barrier height on CPD

Results given in the table indicate the essential dependence of barrier height in these diodes on CPD. Barrier height changes with the nature of the metal in the range of ~ 0.4 eV. Fig. 3 gives the dependence of the height of a Schottky barrier /37 on the work function of the metal for cases of surfaces sheared in a high vacuum [1] and an actual GaAs surface — [2, 3] and this work. In works [1, 3] and in this work the metal is coated by vaporization in a vacuum, in [2] by electrochemical deposition.

We note that in studying the dependence of barrier height on work function φ_m a difficulty will be encountered in selecting values of φ_m for various metals.

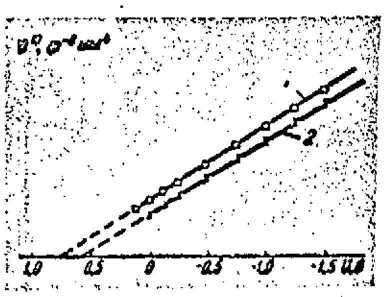

Fig. 2. VFC for Mg/GaAs (111)A and Ag/GaAs (111)A diodes:

1 — Ag; 2 — Mg

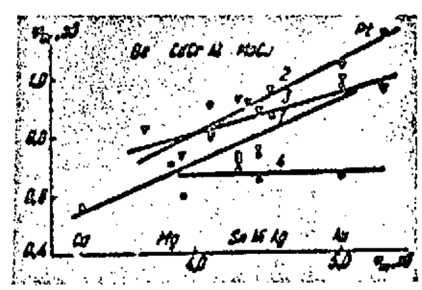

Fig. 3. Dependence of barrier height on work function of the metal:

o — results of this work (orientation (111)A; ∇ — results of [1] (orientation (111)A); 0 — results of [2] (orientation (111)A); ▼ — results of [3] (orientation (110)).

As is known, work function is very sensitive to numerous factors (contamination of the surface, crystalline structure, etc.), in connection with which experimental data on φ_m often varies widely [12]. That experimental points for Ni [13, 14] and Cr [3] fall outside the general rule impelled us to approach selection of φ_m values for these metals critically. In our opinion, the values of the work function of metals in which we were interested (Ni, Cr), as well as Cu and Pt, given in [15] are reliable. The use of values of φ_m, which we determined under similar conditions, led to a significant reduction in the variance between experimental points (in relation to the lines given in Fig. 3).

Let us turn now to the dependence of barrier height on φ_m, obtained by other authors (See Fig. 3). Experimental points for a contact between an actual (etched) GaAs surface and various metals easily fall on straight lines 1 and 2, whose slope coincides with an accuracy to 20%. This shows that the SES system of an etched GaAs surface is practically independent of the degree of vacuum. Line 3 for an atomically-pure GaAs surface is characterized by a lesser (but *) slope.

From the results for electrochemically deposited contacts the authors conclude rigid stabilization of the Fermi level on the metal boundary (line 4). The difference between electrochemically deposited contacts [2, 4] and those produced by vacuum metal vaporization also appears in the orientation dependence of the barrier height.

ANISOTROPY OF BARRIER HEIGHT

The table shows that significant anisotropy of barrier height in the diodes we studied is observed only for Ni/GaAs contacts;

$$\varphi_B(111)B > \varphi_B(110) > \varphi_B(111)A, \quad (2)$$

which agrees well with results for the electrochemical deposition of metal [2]. /38

For the other metals except Ca, barrier height at (111)B exceeded that at (111)A by several hundred electron volts. For Ca a great variance was observed in barrier heights; however, the average barrier height on surface (111)B was slightly less than on other crystallographic planes.

These results indicate that anisotropy of barrier height, as well as the value of φ_B, can be determined by the nature of the metal. As Ni/GaAs contacts differ

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significantly in properties from other contacts, we studied in detail the effect of conditions of production on anisotropy of barrier height in Ni/GaAs contacts. In particular, we studied contacts produced by metal deposition on a GaAs surface, treated in the following manner: semiconductor plates were etched in a standard nitric acid etchant, etching was stopped by the addition of twice-distilled water, then samples were blotted and dried. This treatment of the surface does not remove the oxide from the GaAs surface, leading to increase in parameter n to 1.2 – 1.35. It was shown that pronounced anisotropy of barrier height is maintained (within limits of 0.15 – 0.20 eV).

MODEL OF METAL/GaAs CONTACT

The dependence of barrier height on work function of the metal for vacuum-deposited contacts indicates lack of stabilization of the Fermi level at the metal/GaAs contact. At the same time this dependence is weaker than would follow from the Schottky model. Thus, CPD is partially screened by the charge of the SES on the interface. In fact, with a change in work function to $\Delta\varphi_m \simeq 1.8$ eV, barrier height changes to $\Delta\varphi_B \simeq 0.4$ eV. A rather high value of $\Delta\varphi_m$ indicates that the model, assuming an absence of SES in a large part of the forbidden zone of GaAs [7], is not adequate.

Our experimental results correspond much better to the model of Cowley and Sze [16] assuming the presence of acceptor type SES in a large part of the forbidden zone of GaAs and Si. At the same time, experiments conducted on p-Si [13] indicate that a model with a SES system of the same type is inadequate for complete description of the metal/Si contact. It is interesting to note that on the free GaAs surface, as on the free Si surface, acceptor and donor SES systems are observed [17, 18]. Thus, SES systems of a free Si surface and the Si/metal interface are basically the same. If this is also valid in relation to GaAs, then the GaAs/metal contact must contain acceptor and donor type SES. The studies we conducted of p-GaAs/metal contacts agree with this.

Employing the formulas given in [16] and the estimate of parameters of the intermediate layer for Schottky diodes with similar n parameters [3], according to the slope of line 1 in Fig. 3, we calculated the density of SES at the metal/GaAs contact. The value we obtained ($4 \cdot 10^{13}$ cm$^{-2}\cdot$eV^{-1}) is close to the value $3 \cdot 10^{13}$ cm$^{-2}\cdot$eV^{-1}, determined on the basis of experimental data [3] (line 2 in Fig. 3).

There is interest in comparing the properties of an atomically-pure GaAs surface and one covered with metal. An extremely noteworthy fact, in our opinion, is that the SES density on an atomically-pure GaAs surface is inadequate to stabilize the Fermi level. As shown by Scheer and Van Laar [19], the CPD between n- and p-GaAs can vary widely (to 0.7 – 1 eV), which indicates relatively low SES density (in comparison with Si) on an atomically-pure GaAs surface. This fact is also reflected in the properties of the contact between an atomically-pure GaAs surface and metals. Detailed correlation does not, of course, indicate identity of SES systems of free and metal-covered semiconductors. However, evidently, in some cases the SES system of a free surface is changed only very slightly during the deposition of metal. In particular, work [20] shows by the field effect method that a rapid SES system for an actual silicon surface changes very little during the deposition of a rather thick (several tens of angsts) film of various metals. The question of how much the SES system of the original semiconductor surface is changed during metal deposition must be resolved for each specific case, taking into account the original properties of the semiconductor surface, the methods of deposition of the metal (vacuum deposition, electrochemical or chemical deposition, etc.) as well as the individual characteristics of each metal.

CONCLUSION

The experimental results obtained in this work show that in the formation of a Schottky barrier at a GaAs/metal contact, both the CPD and SES of the interface are important. The latter weaken the dependence of the barrier height on CPD; this effect is observed in the large energy interval of the forbidden zone and not only in sections it determines [7]. Basic laws observed for vaporized-on metal/GaAs contacts seem to support the assumption that an acceptor and donor type SES system is present in the contact; this system is typical of a free gallium arsenide surface.

Discrepancies in the results for contacts produced by various methods [1-5] can indicate the effect of the method of metal deposition on the properties of the contact either in connection with the dependence of properties of metal film on the method of its deposition or changes in properties of the semiconductor surface. This does not exclude the possibility of the effect of the individuality of metals in the formation of a Schottky barrier. This is indicated by the orientation dependence of barrier height, particularly for a Ni/GaAs contact. These characteristics demand care in analyzing the properties of the interface.

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16. Abstract

Study of the Schottky barrier at the contact between an etched n-GaAs surface and various metals (Ca, Mg, Sn, Ni, Ag and Au). The obtained dependence of the barrier height on the contact potential difference (CPD) indicates that a significant role is played by the CPD and the surface electron state charge in the formation of the barrier. Partial screening of the CPD was observed in a wide forbidden band energy range (the Fermi level at the boundary was displaced approximately 0.4 eV). A relatively weak dependence of the barrier height on the crystallographic orientation of GaAs was observed for most of the investigated metals, while a significant orientation dependence was observed for an Ni-GaAs contact. A.B.K.

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